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The Chronopotentiometry of Bismuth

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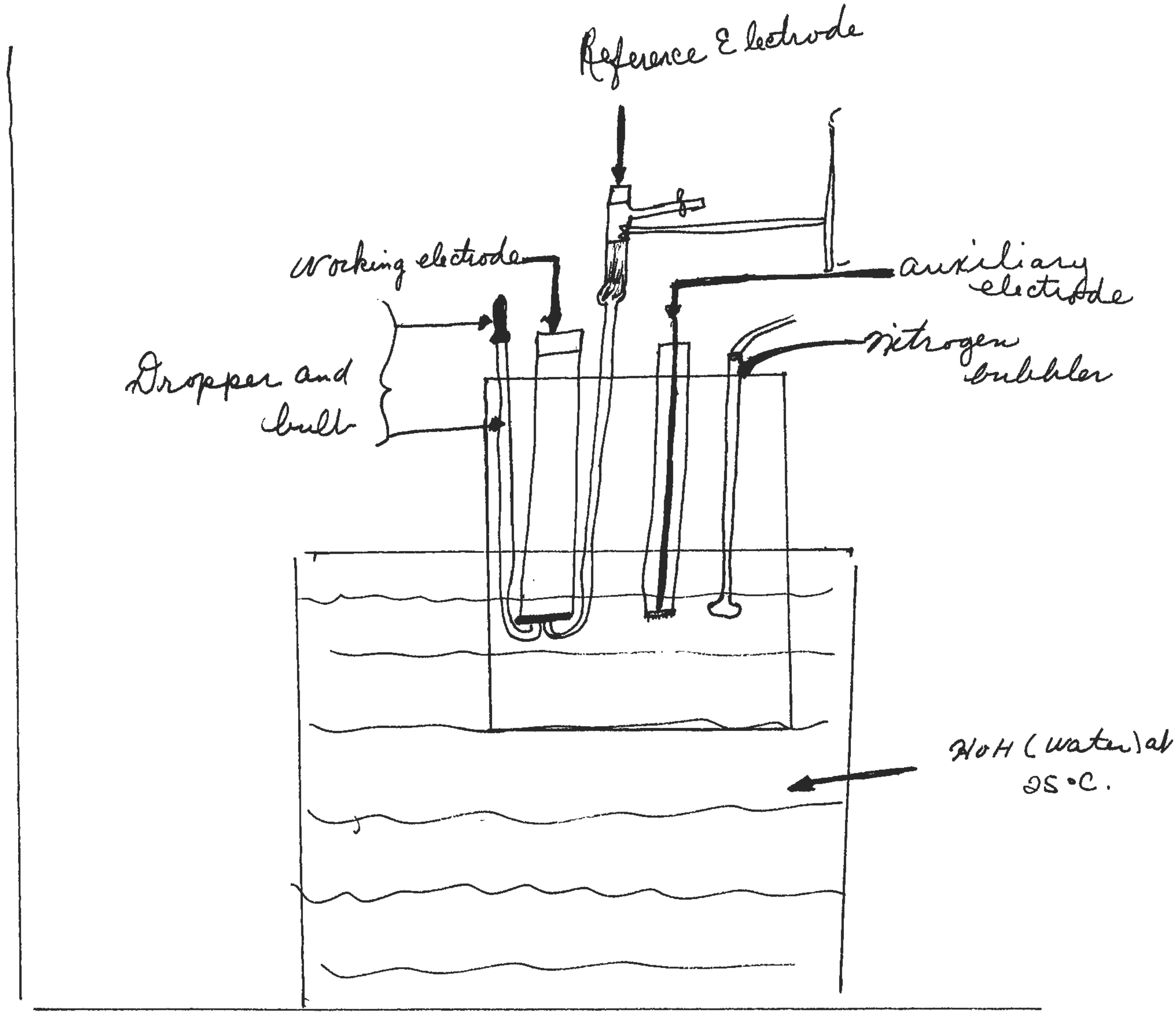
The Chronopotentiometry of Bismuth

Whenever a constant current electrolysis is performed without stirring, the potentials of the electrodes change with time because the concentrations change at the surfaces of the electrodes. The principle of chronopotentiomety is based upon the idea that since the current is kept constant, the electrolysis proceeds at a constant rate. When the electrolpis circuit is closed, the concentrations of the substances taking part in the electrochemical reaction at the surface of the electrode start to vary. The electrode takes up the equilibrium potential as given by the Nernst equation provided the reaction is reversible. If the transport of the substances is fast enough, the variations only occur for a certain period, after which a steady state is reached, and the electrode potential becomes constant. In the absence of convection, the transport is entirely due to diffusion. Since the transport is not enough to compensate for the decrease in concentration at the surface of the electrode, this concentration decreases until it reaches zero. The electrode potential, which is given by the Nernst equation changes abruptly when the concentration becomes zero. The time at which the abrupt change in the potential occurs is known as the transition time or τ (Ref. 1 - pp. 314-315). Through the use of Fick's Law of Diffusion, the Sand equation, which provided the basis for the work explained in this paper, can be derived; $i\sqrt{\tau} = kc$ where i is the current in amperes, τ is the transition time, C is the concentration of the solution being electrolyzed, and the "k" term is dependent upon the diffusion coefficient of the electroactive species.

The apparatus used consists of an approximate constant current source consisting of a high voltage source in series with high resistance, an automatic recorder, and an electrolytic cell which consists of a working electrode, auxiliary and reference electrodes, a nitrogen bubbler, a dropper and bulb, and a constant temperature tank. The auxiliary electrode, a strip of platinum wire, is isolated from the rest of the cell. The working electrode is a flat electrode which contains a platinum disc. Hydrogen or oxygen is evolved at the platinum electrode. These gases would probably interfere with the operation of the working electrode if a one compartment cell were used (Ref. 2 - p. 395). The potential of the working electrode is measured with respect to the reference electrode (Mercury electrode), and the auxiliary electrode completes the circuit (Ref. 2 - p. 391). The supporting electrolyte used in this instance is hydrochloric acid. Dissolved oxygen may be reduced, and its presence generally makes it difficult to study cathode phenomena. The solution is freed from oxygen by bubbling an inert gas (nitrogen) through it (Ref. 1 - p. 140). The dropper and bulb are used to remove air at the surface of the working electrode, and

Electrolytic Cell Used



the constant temperature tank is used as a temperature control for solutions of varying formalities because the diffusion coefficient, which is a vital part of the Sand equation, is temperature dependent.

Through the study of various reactions and through the study of the chemical properties of various elements, one can predict the most probable electrolytic reaction. A chronopotentiogram of copper was made as a preliminary test determination. As indicated in graph I., which is the result of the copper determination the reaction proceeds in two steps. The equations explaining the two steps of the graph are probably

$$\begin{array}{l} Cu^{++} + e^- \longrightarrow Cu^+ \\ \underline{Cu^+ + e^- \longrightarrow Cu^\circ} \\ Cu^{++} + 2e^- \longrightarrow Cu^\circ \end{array}$$

At the outset of this experiment the theoretical prediction was that a bismuth solution would electrolyze in one step to form bismuth metal

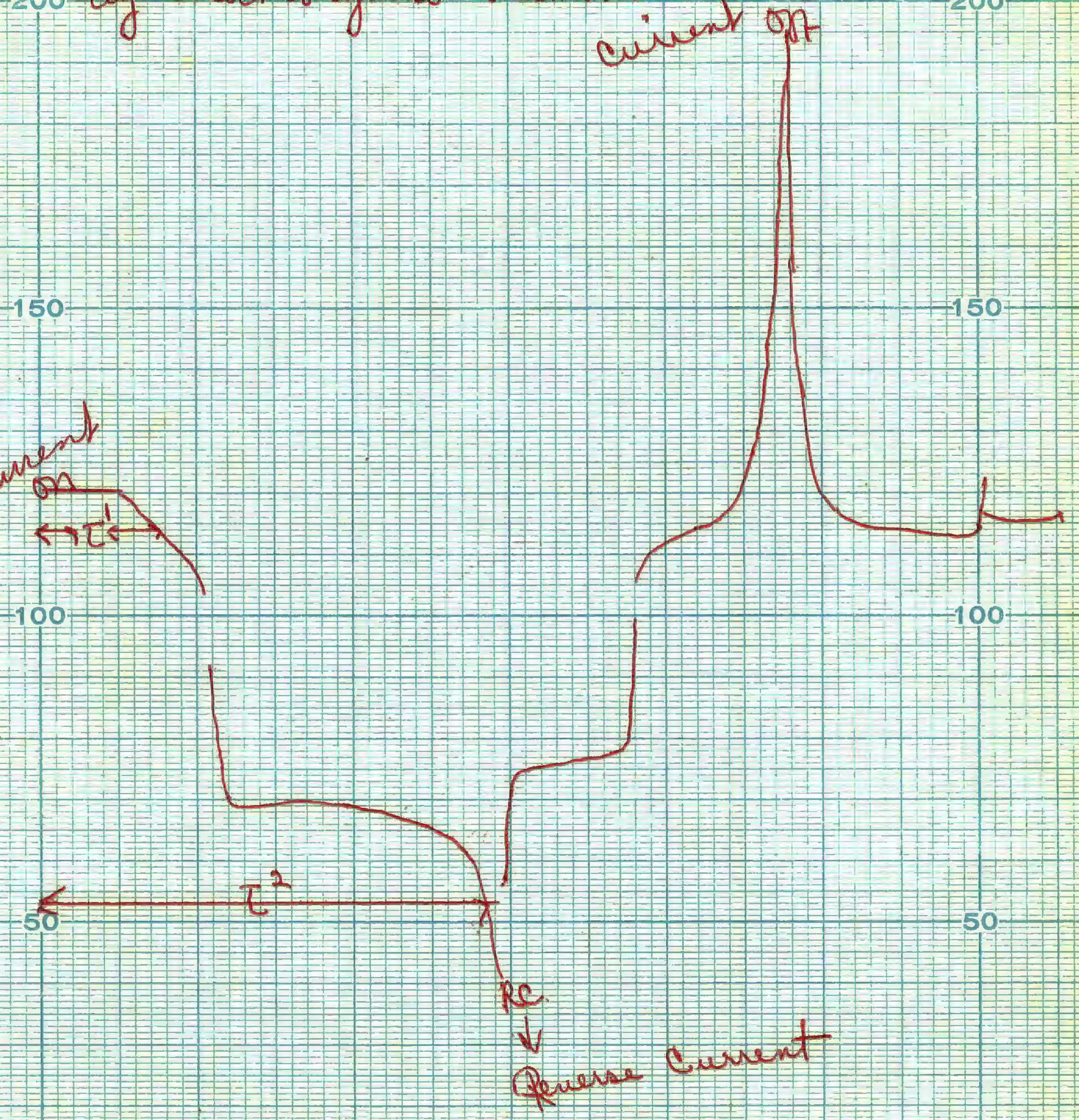
$$Bi^{+++} + 3e^- \longrightarrow Bi^\circ.$$

The succeeding data indicated that the theoretical prediction is correct. Graph III. shows the one break in the curve of a .005 F Bi^{+++} solution indicating a one-step reduction process.

Before the Sand equation could be applied

Graph I.

This graph illustrates the two breaks in the curve when Cu^{++} is converted to Cu° by electrolytical methods.



to the graphs, a method for the calculation of τ values had to be found. There are many accepted methods which are employed for the calculation of τ values, but the one that gave the best results in this experiment was that of locating the steepest inflection point as indicated in graph 9.

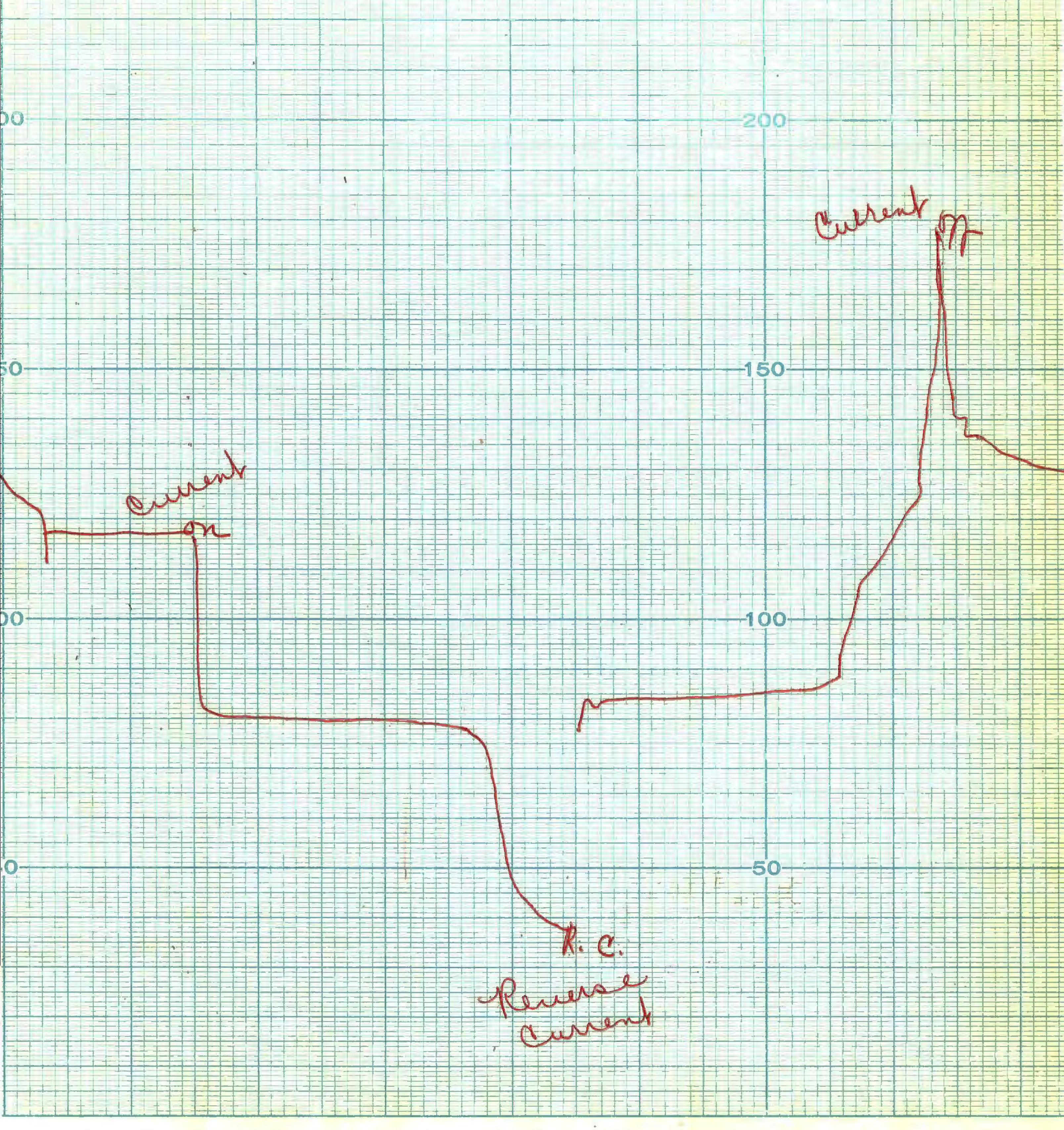
Generally, $i\tau^{\frac{1}{2}}$ values were constant for solutions of the same formality (.01F and .005F). This is indicated by the following values:

τ is in inches of chart paper. These are the most convenient units since the recorder was pre-set to give representations of 5 inches of chart paper per minute. Thus, each inch represents twelve seconds.

.01 F sol.

i (in μamps.)	$i\tau^{\frac{1}{2}}$ (μamps inches$^{\frac{1}{2}}$)
1.27×10^3	2.1×10^3
1.27×10^3	2.2×10^3
1.80×10^3	2.2×10^3
1.80×10^3	2.2×10^3
9.00×10^2	2.2×10^3
2.54×10^3	2.3×10^3
2.54×10^3	2.3×10^3
1.291×10^3	2.3×10^3

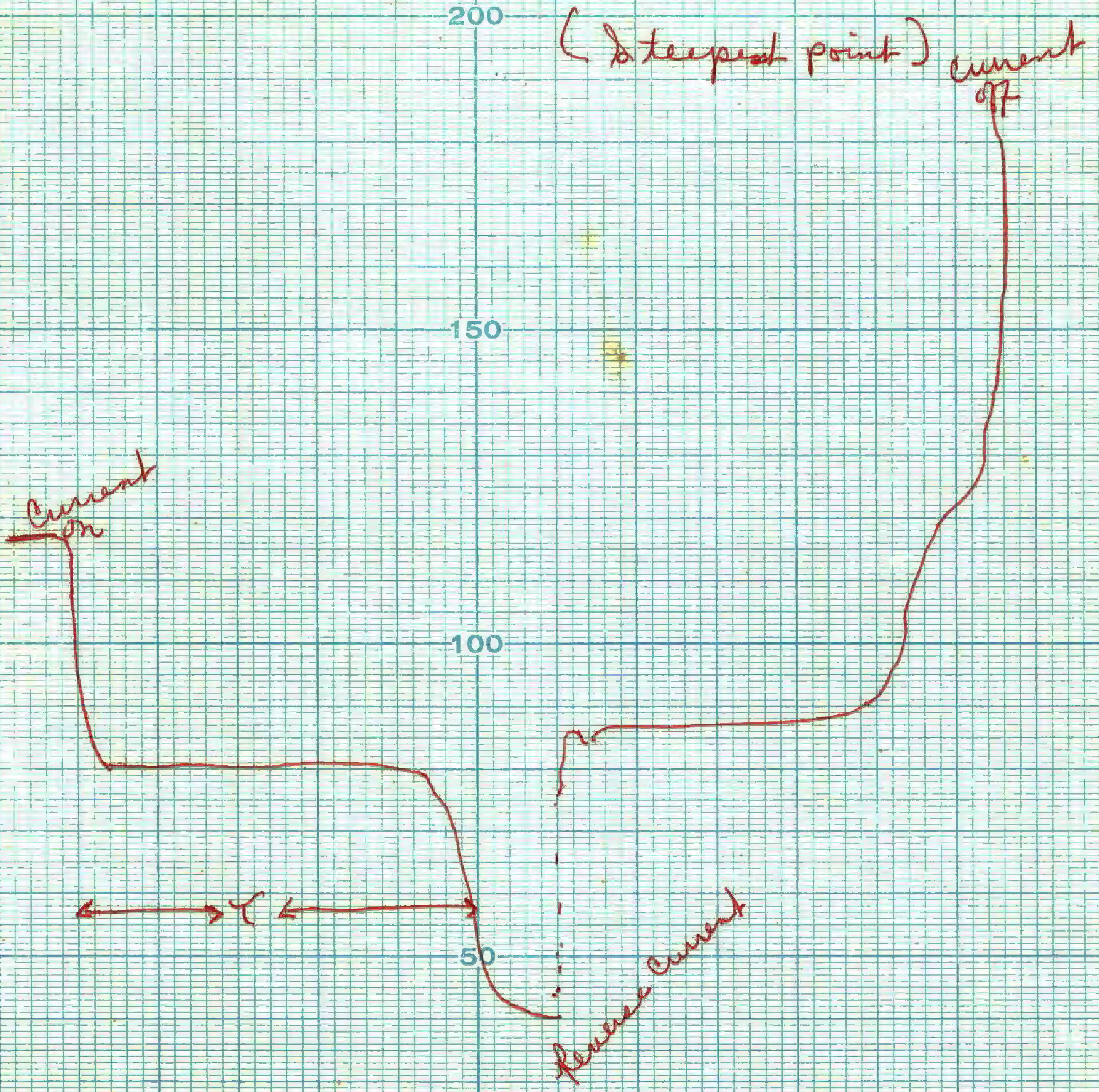
Graph II. One-Step $Bi^{+++} + 3e^- \rightarrow Bi^0$



Calculation of τ

This is the method used in this experiment,

(Steepest point)



.01 F sol. continued

i (in μamps.)	$i\tau^{\frac{1}{2}}$ (μamps inches$^{\frac{1}{2}}$)
1.291×10^3	2.2×10^3
1.291×10^3	2.2×10^3
9.012×10^2	2.2×10^3

The average deviation is 4%.

.005 F sol.

i (in μamps.)	$i\tau^{\frac{1}{2}}$ (μamps inches$^{\frac{1}{2}}$)
1.282×10^3	1.26×10^3
1.282×10^3	1.25×10^3
1.282×10^3	1.25×10^3
9.110×10^2	1.24×10^3
9.110×10^2	1.24×10^3
6.580×10^2	1.23×10^3
6.580×10^2	1.25×10^3

The average deviation is 8%

$i\tau^{\frac{1}{2}} = kc$ does not apply exactly to this experiment. For the .01F solution $k = 2.2 \times 10^5$. For the .005 F solution $k = 2.5 \times 10^5$. This indicates a 15% deviation which, although is not good, is not too unreasonable.

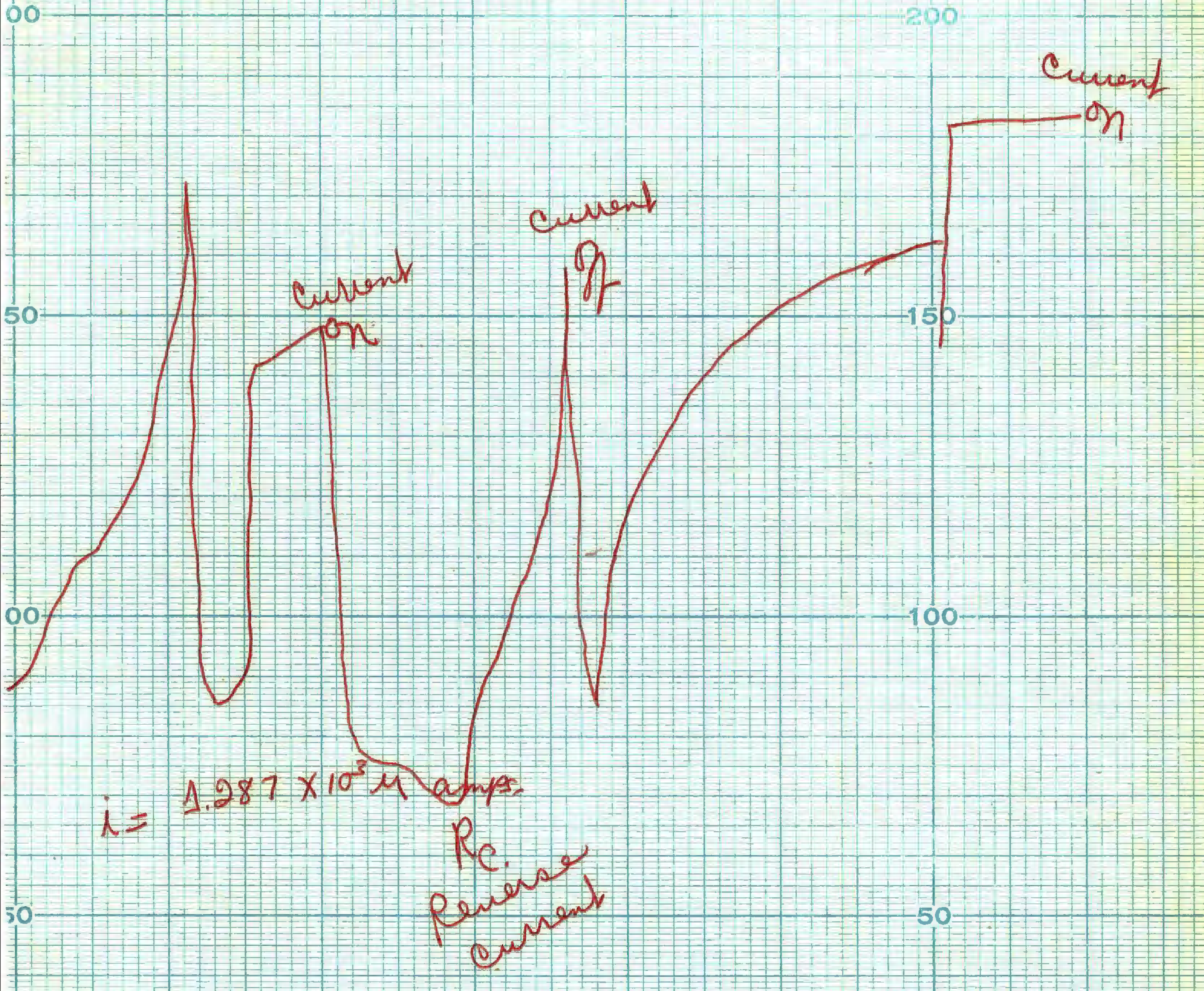
There appeared rather irregular graphs for the .001 F solution. It was mentioned earlier in the paper that the evolution of hydrogen often interferes with the operation of the working electrode so that accurate indication of the reaction involved in the electrolysis can not be determined. This is particularly evident with the .001 F solution. The irregular waves as indicated in graph IV. are possibily results of high hydrogen production. This might also account for the non-application of $i\tau^{\frac{1}{2}} = kc$ to the .001 F solution. Values for the .001 F sol. are

i (in μ amps.)	$i\tau^{\frac{1}{2}}$ (μ amps in$^{\frac{1}{2}}$)
2.355×10^2	2.35×10^2
$2{,}365 \times 10^2$	$2{,}35 \times 10^2$
$4{,}730 \times 10^2$	$2{,}35 \times 10^2$
4.730×10^2	2.35×10^2
$6{,}590 \times 10^2$	$2{,}\overset{56}{\cancel{82}} \times 10^2$
$2{,}363 \times 10^2$	$2{,}80 \times 10^2$
$2{,}363 \times 10^2$	2.80×10^2
$1{,}700 \times 10^2$	3.20×10^2
1.700×10^2	3.20×10^2

If only the first four values are considered, $k = 2.4 \times 10^5$ which is fairly in accord with the other two values (2.2×10^5 and 2.5×10^5). However, if all of the values are considered there is a 22% average deviation between the individual values of $i\tau^{\frac{1}{2}}$. The average k value is 2.6×10^5 which also falls within the range of the other values. There is a 17% average deviation between these three k values (2.2×10^5, 2.5×10^5 and 2.6×10^5).

If the only processes are the plating and the dissolving of bismuth and if the current is reversed

Graph IV. .001 F Solution

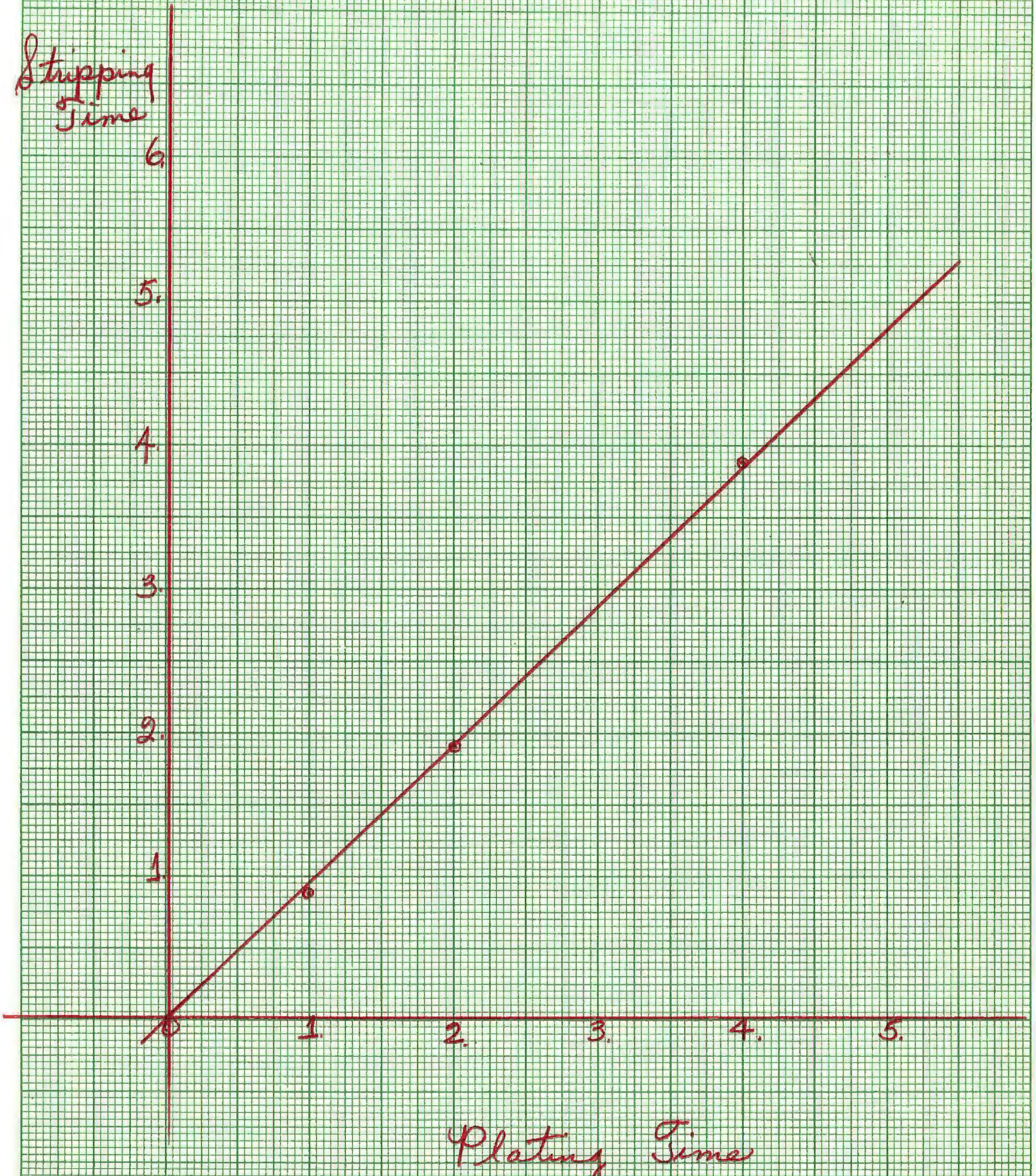


before the transition time, the time required to strip the deposit should equal the deposition time. Then a graph of plating time versus stripping time should increase linearly with a slope of 1 (one) going through the origin. In order to test the validity of this assumption, determinations were made of stripping times at various plating times. The results of these determinations are given in graph V.

It was indicated in the references cited earlier that excess oxidation of the platinum electrode deposits a thin film of platinum oxide on the electrode. As a result, part of the succeeding τ value would result from the stripping of platinum oxide as well as from the deposition of bismuth. An experiment was performed which was designed to determine the effects of oxidation of the electrode for varying lengths of time. The oxidation was allowed to proceed to .11 V, .58 V, .68 V, 1.04 V, and 1.06 V. Then the stripping time for the succeeding determination was made. In each instance, a constant plating time of three inches or 36 seconds was used as the control. If the oxidation had had no effect then the stripping time would have been 3 inches or 36 seconds in each instance. Below are the results of this experiment:

Voltage	Stripping Time for Succeeding Determination Inches
.11 V	2.750"
.58 V	2.399"
.68 V	2.800"
1.04 V	2.000"
1.06 V	1.850"

Graph V. Plating Time vs. Stripping Time



Plating Times and Stripping Times are in inches of chart paper.

This indicates that oxidation of the platinum electrode possibly causes invalid results to be obtained. This might account partially for the slight discrepancy in the $i\tau^{\frac{1}{2}} = kc$ determinations.

Summary

1. $i\tau^{\frac{1}{2}} = kc$ (According to determinations made in this paper) does not apply to this reaction - $Bi^{+++} + 3e^{-} \rightarrow Bi^{\circ}$.

2. Oxidation of the platinum electrode affects the determination of τ values.

3. High hydrogen production affect the results.

4. A graph of plating time vs stripping time increases linearly.

List of References

1. — Charlot, Bradoz-Lambling, and Tremillon, *Electrochemical Reactions*, 1962, Elsevier Publishing Company, New York, pp. 140, and 314-315.

2. — Delahay, *New Instrumental Methods in Electrochemistry*, 1954, Interscience Publishers, Inc., New York, pp. 351, 391, and 395.